

PANI /SPANI copolymer for the protection of iron against corrosion

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Interesting protection of iron against corrosion was obtained by electropolymerization of a polyaniline (PANI) layer in phosphoric medium, in presence of metanilic acid (MA). The use of phosphoric acid instead of another organic or inorganic acid (for instance, oxalic acid which was currently used) increased the protection time of an order of magnitude; this time is doubled by the addition of 0.05 M of MA [1]. Since the main effect of the polymer layer is to stabilize the iron oxide passive layer, the role of phosphoric acid can be easily explained by the incorporation of phosphate ions in the passive layer which becomes therefore particularly protective.

The role of MA is more debatable. It is known for some years [2] that a copolymer (SPANI) of aniline and MA (3-aminobenzenesulfonic acid) can be formed, MA being introduced in the polymeric chain via its amine nitrogen; substituted aniline takes partially the place of aniline. In spite of the low MA concentration, the presence of new features in the optical spectra allows to characterize polymeric units containing sulfonated aniline. To understand the structure of these PANI /SPANI polymers, layers electro polymerized on platinum in presence of a high MA concentration were studied using optical spectroscopy.

Experimental

In [1], PANI was potentiostatically deposited on a rotating iron electrode from a solution composed of 1.7 M H_3PO_4 , 0.05 M MA, 0.3 M aniline at pH 0.5, after preliminary treatments in the solution devoid of aniline to form a strong oxide /phosphate passive layer. The MA /aniline ratio was progressively enhanced but to form a polymer layer, it cannot exceed 1 and in these conditions, the deposition is preceded by several hours induction lapse.

The protection against corrosion offered by the PANI /SPANI layers is characterized by the iron open circuit potential, V_{oc} , in a corrosion test solution (CTS): 0.1M K_2SO_4 with an admixture of H_2SO_4 up to the chosen pH.

To optically characterize the films deposited on platinum in presence of a higher MA /aniline ratio, phosphoric acid is replaced by sulfuric acid in which the solubility is better (without modify the PANI structure).

Results

Absorption spectra of films polymerized on Pt in 0.15 M aniline + 0.2 M MA are given in figure 1. These spectra are very different of the PANI ones [3]; they are characteristic of an heterogeneous structure, with together conducting segments (isolated polarons at 2.7 eV, free-carriers at 1 eV) and insulating oxidized segments (excitonic absorption around 2.2 eV). The strong excitonic absorption at 2.45 eV cannot be assigned to usual PANI structure and we assumed that oxidized units form around the sulfonated aniline rings, and that they are very difficult to reduce. It was shown [4] that the breakdown of passivity corresponds to the disappearance of optical features characteristic of oxidized units. The second kind of oxidized units must therefore be

responsible of the good performances of PANI /SPANI layers.

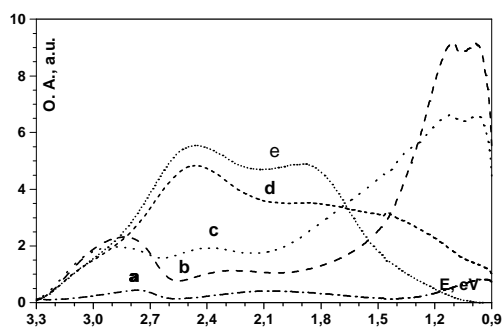


Figure 1: Optical absorption of PANI /SPANI films on Pt polarized in CTS (pH 2) at potentials: -400 (a); -200 (b); 0 (c); 200 (d); 400 (e) mV/SSE (saturated sulfate electrode)

Figure 2 shows corrosion tests in CTS (pH 1); at the beginning of test, $V_{oc} = V_{pass}$, iron passivity potential. A very sharp fall down to V_{corr} , iron corrosion potential, corresponds to the breakdown of the underlying passive layer. The corrosion strength is characterized by the time spent before the fall. The passive layer formed in phosphoric solution without aniline, according to the routine described in [1], lasts 29 s in CTS (which displays the intrinsic good quality of the passive layer); the formation of a PANI layer by addition of 0.25 M aniline (without MA) leads to plot b. The total anilinium concentration of 0.25 M is kept when MA is added, leading to plots c (MA /aniline ratio identical to [1], i.e. 1 /6) and d (maximum MA /aniline ratio, i. e. 0.125 M aniline / 0.125 M MA).

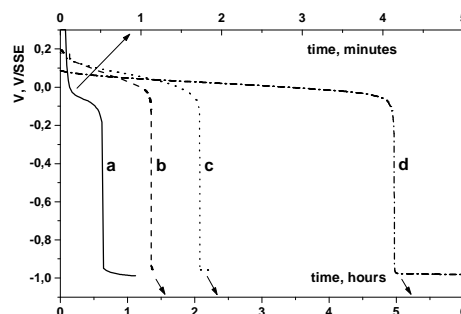


Figure 2: Comparaison of V_{oc} during the immersion in CTS (pH 1) of iron covered by: a, passive layer; b: PANI layer; c and d: PANI /SPANI layers

Conclusion

These first results show the protective properties of PANI /SPANI layers polymerized on iron. However, in the present experiments all the electrodeposition parameters (rotation speed, temperature...) were not quite optimized which allows to expect still much better protection times.

References

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